Effect of Grinding on Porosity and Surface Area of Coal[a]

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Introduction

A great deal of information may be gained about the porosity of coal by studying the gas release behavior during grinding. We believe that this gas was stored in the closed porosity of the coal. This study focuses on describing the closed porosity of coal by considering the gas release rates, total gas volume, density, and surface area of coal during ball milling.

We suggest that most of the gases released during ball milling were either trapped or produced in the closed pores during coalification. Therefore, the composition of the gas provides information about the coalification processes. In this paper we discuss the significance of our composition measurements with respect to the coalification process.

Experimental

Two coals of widely differing rank were selected for this study: one was a lignite from the Fort Union Bed near Savage, Montana (PSOC-837);[b] and the other was a medium volatile bituminous coal (MVB) from the Beckley seam near Duo, West Virginia (PSOC-985).[b]

Prior to ball milling, the coals were pre-ground to minus 20 mesh (U.S. Standard screen, 840 μm opening size) in a wheel-type-pulverizer. The pre-grinding was done in a nitrogen filled glove box. The coal (350 g) was transferred in the N_2 atmosphere to a 1.8 L steel ball mill, and then the mill was evacuated and back-filled with helium. During the ball milling, coal and gas samples were withdrawn. Gas was extracted through a rubber septum mounted in the end of the mill and coal powders were extracted from the mill during operation with a scoop inserted along the axis of rotation through a hole plumbed with a rotary union and ball valves to maintain the atmosphere and pressure.

Gases (H_2, CO, CO_2, N_2 and C_1 to C_4 hydrocarbons) were analyzed using a dual column gas chromatograph with helium ionization detectors.

Results and Discussion

As shown previously for lignite,[1] fracture during ball milling proceeds first through the weakest materials characterized by large (up to 5 μm) pores, resulting in large comminution rates initially. As comminution continues, stronger materials characterized by smaller pores are fractured, resulting in lower comminution rates. The change in porosity with time is shown qualitatively in the micrographs of lignite particles in Figure 1. Notice that the visible porosity decreases with increased ball milling time.

Many of the pores affected by the comminution process were initially closed. When the closed pores are opened, the density and surface area of the coals increase, as shown by Table 1.

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(b) Pennsylvania State University's coal sample bank number.

TABLE 1. Density and surface area of coals at indicated ball milling times.

Coal	Ball Milling Time, min	Density,[a] g/cc	Surface Area,[b] m^2/g
Medium volatile bituminous	0	1.365	0.68
	15		1.92
	90		5.28
	180		7.73
	300		8.56
	420	1.404	9.05
Lignite	0	1.476	0.97
	90		1.20
	180		1.60
	420	1.490	2.49

(a) based on helium displacement in a null pycnometer
(b) based on N_2 adsorption at 77 K

Making a small correction (0.30 m^2/g) for the increase in geometrical surface area, and assuming that cylindrical pores were being opened during ball milling, the pore diameter, $d = 4\ \Delta V/\Delta S$ (ΔV = increase in pore volume, ΔS = increase in surface area). The pore diameters were calculated to be 10 and 21 nm for MVB and lignite, respectively, indicating the diverse pore structure of these two coals.

As these pores were opened during ball milling, gas was released. The composition and quantity of gas released after 420 minutes of ball milling is shown in Table 2. Using the total gas released and the open pore volume increase after 420 minutes of ball milling, concentrations in terms of gas volume to pore volume ratios were 2.4 and 57.2 for MVB and lignite, respectively. The gas was stored inside the pores in the adsorbed or gaseous state, and it is apparent that the coalification conditions under which the gas became incorporated into the pores was greatly different for the two coals.

TABLE 2. Gases released from medium volatile bituminous coal and lignite after 420 minutes of ball milling.

Coal	Gas, ml (STP)/g Coal					
	N_2	CO_2	CO	CH_4	H_2	Total
MVB	4.66×10^{-2}	2.46×10^{-3}	9.12×10^{-5}	3.16×10^{-5}	1.28×10^{-4}	4.93×10^{-2}
Lignite	0.326	3.81×10^{-2}	1.68×10^{-3}	(a)	(a)	0.366

(a) too small to measure

The release rate of gas from both coals increased markedly when ball milling began, as shown by Table 3. The release rate also changes with time during ball milling, and the average rates are given for specific milling times. An example of how the release rate changes with time is shown for CO_2 in Figure 2. The other gases are released in a similar way.

TABLE 3. Average gas release rates for lignite and medium volatile bituminous coal.

Time Period	Medium Volatile Bituminous	Time Period	Lignite
	(ml/g-min)		(ml/g-min)
Before milling (16 hr)	4.4×10^{-7}	Before milling (16 hr)	2.9×10^{-6}
During milling		During milling	
0 to 4 min	2.2×10^{-3}	0 to 30 min	1.1×10^{-4}
60 to 180 min	1.4×10^{-5}	60 to 120 min	6.3×10^{-4}
		120 to 240 min	1.3×10^{-4}
Stopped milling (16 hr)	1.2×10^{-5}	Stopped milling (88 hr)	3.1×10^{-5}
Restarted milling		Restarted milling	
180 to 300 min	undetermined	240 to 300 min	undetermined
300 to 420 min	1.3×10^{-5}		
		Stopped milling (160 hr)	9.5×10^{-6}
		Restarted milling	
		300 to 420 min	2.7×10^{-4}

In general, the rate of gas release is expected to decrease with time because comminution rate generally decreases with a decrease in particle size, and particle size decreases with time during milling. A marked decrease in release rate is expected as more and more coal particles decrease below a critical diameter, that is a diameter small enough that all closed porosity has become opened. A second major perturbation to the generally expected release rate occurs due to a change in the preferential mode of comminution. This phenomenon can result in either an increase or decrease in the rate of opening of closed porosity along with the resultant increase or decrease in gas release rate.

It is apparent that the critical diameter of most of the MVB particles had already been reached at 60 minutes of ball milling because after that, the release rates were almost unaffected when ball milling was stopped and then restarted again (Figure 2, Table 3). On the other hand, the particles of lignite had not decreased to the critical diameter even after 300 minutes of ball milling. This conclusion is reached because when ball milling was stopped, the release rate decreased significantly, and when ball milling was restarted, the release rate increased again (Table 3). We suggest that the critical diameter of MVB is larger than lignite based on release rates and ball milling times. We also suggest that the particle diameters of much of the lignite were still larger than the critical diameter even after 420 minutes of ball milling based on the gas release rate at 300 to 420 minutes (Table 2). We know that after 420 minutes of ball milling, 97.5% of the lignite particles were minus 400 mesh (38 μm) and, therefore, suggest that the critical diameter was less than 38 μm. This difference in critical diameter of particles and the pore diameters calculated earlier suggests that lignite had shorter and larger diameter closed pores and MVB had longer and smaller diameter closed pores.

It appears that a change in the preferential mode of comminution caused the gas release rate from lignite to increase by a factor of nearly six after 60 minutes of ball milling (Figure 2, Table 3). As discussed before for lignite, comminution in the early stages of ball milling proceeds preferentially through material characterized by open pores up to 5 μm which did not release gas. But after

60 minutes of ball milling, comminution proceeds preferentially through material characterized by closed pores with calculated diameters of about 21 nm which when opened released gas, thus increasing the gas release rate. The decrease in rate at 120 minutes and subsequent increase again at 300 minutes could be caused by a combination of changes in comminution rate, reduction of the size of particles below critical diameter, and preferential modes of comminution. With MVB, comminution proceeded through materials characterized by closed pores with calculated diameters of about 10 nm with no change in preferential mode of comminution recognized.

The composition of the gases released from the closed pores of these test coals suggests some interesting conclusions about the coalification process. These coals had been stored in air for four years prior to testing for gas release during ball milling. Concentrations of N_2, CO_2, CO and H_2 (Table 2) were not greatly different than concentrations measured in freshly mined coal[2-4] but, unlike freshly mined coal, which consistently contains 80 to nearly 100% by volume CH_4,[2-4] there was hardly any CH_4. The CH_4 is generally believed to be produced by anaerobic digestion of plant remains during the initial stages of coalification.[3] If this is true, the CH_4 was excluded, by some mechanism, from the closed porosity of the coal. Perhaps the anaerobic digestion occurred only in localized areas, instead of throughout the whole seam, and CH_4 was diffused to the open porosity, but not generally to the closed porosity of coal. Then, after coal is mined and stored in a gas not containing CH_4, the CH_4 is slowly diffused out of the open pores and the gas which is stored in the closed pores remains.

Conclusions

From gas release, density, and surface area measurements we have concluded the following:

1. The closed pores of the medium volatile bituminous (MVB) coal are about 10 nm in diameter and the closed pores of the lignite are about 21 nm in diameter assuming cylindrical channels.

2. The concentrations of adsorbed and gas phase gases inside the closed pores are 2.5 and 57.2 [gas volume (STP) to pore volume ratios] for the MVB and the lignite, respectively, indicating greatly different coalification conditions during pore formation.

3. The closed pore volume in both coals decreases with a decrease in particle size during ball milling, but the particle size at which the closed pore volume becomes insignificant is larger for MVB than for lignite, that particle size for lignite being less than 38 μm.

4. The closed pores of these coals contain very little CH_4, which probably indicates that the CH_4 produced during the early stages of coalification was produced in localized areas rather than throughout the seam.

References

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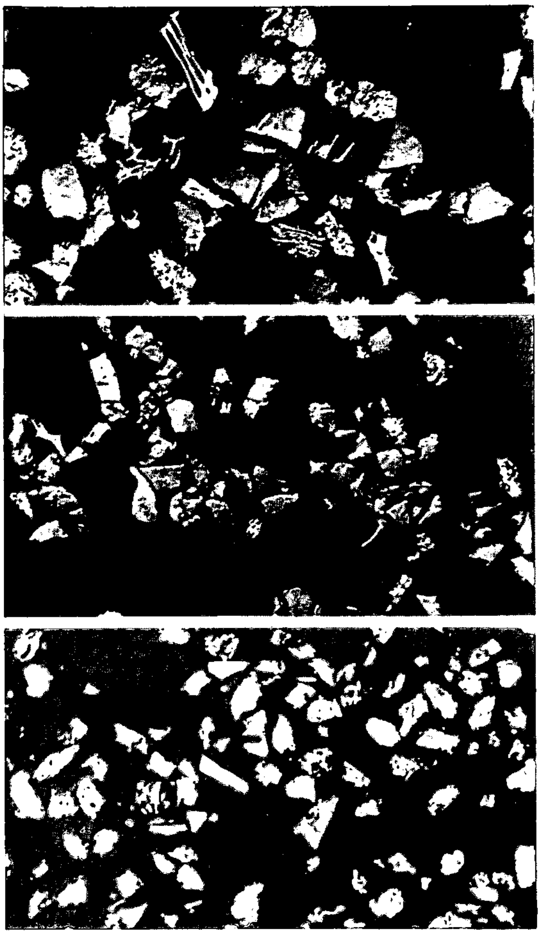
BALL MILL GRINDING PRODUCT: 20-30 μm



15 MINUTES

60 MINUTES

420 MINUTES

50 μm

FIGURE 1 MICROSTRUCTURE OF LIGNITE GRINDING PRODUCTS AT VARIOUS TIMES SHOWING DECREASED VISIBLE POROSITY WITH INCREASED TIME

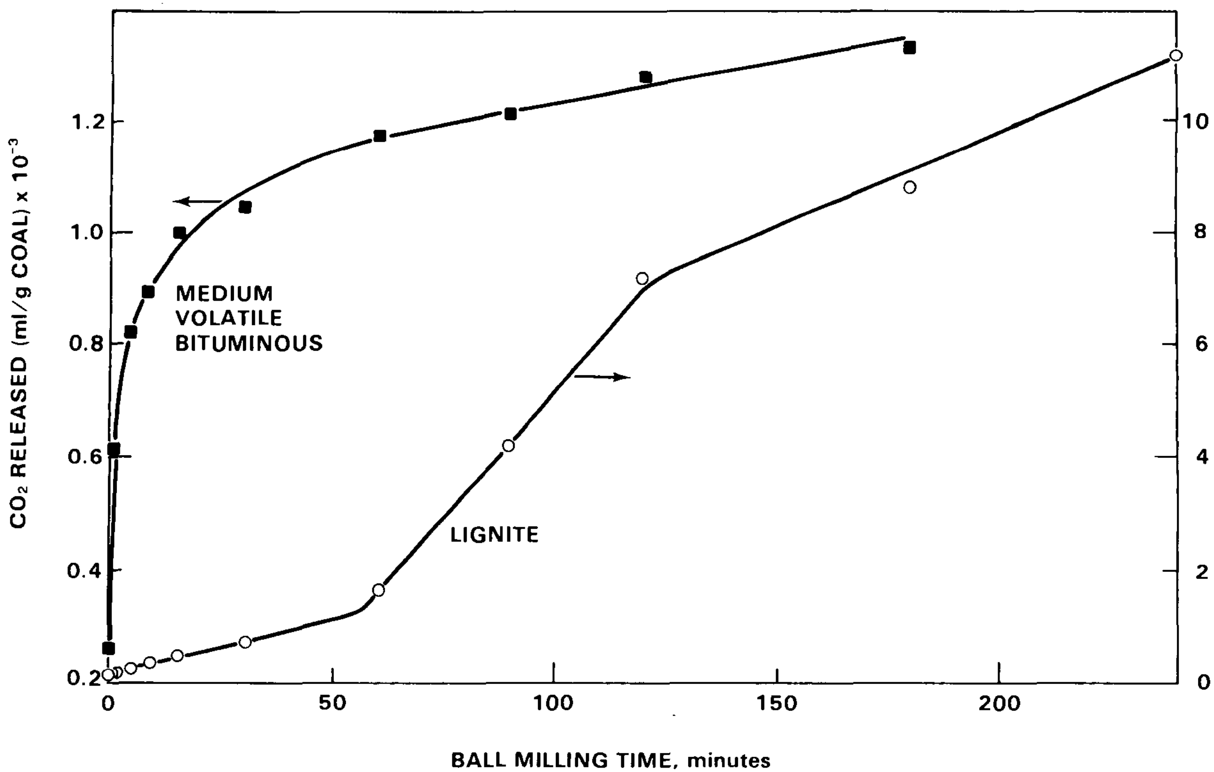


FIGURE 2 THE RELEASE OF CO_2 FROM LIGNITE-○ MEDIUM VOLATILE BITUMINOUS-■ COAL VERSUS BALL MILLING TIME